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(71) Applicants

Dr. Adam Müller,  
Mainburger Str. 15,  
8421 St. Johann/  
Hallertau,  
Germany.

(72) Inventors

Dr. Adam Müller

(74) Agents

Eric Potter & Clarkson,  
14 Oxford Street,  
Nottingham.

(54) Process for obtaining hulupones from lupulones

(57) A process for obtaining hop extracts comprises adding adsorbents to hop products which contain alpha-acids and ground, crushed or ruptured lupulin seeds, or such hop products which are in the form of extracts, treating the mixture obtained with CO<sub>2</sub> in a closed pressure vessel at a supercritical temperature and under a pressure of from 50 to 600 bars, reducing the pressure of the CO<sub>2</sub> leaving the pressure vessel whereby a base extract comprising hop oils and lupulones is precipitated, mixing the lupulones with adsorbents, converting the lupulones to bitter-tasting hulupones by oxidation and treatment with CO<sub>2</sub> under pressure, and removing undesirably accompanying substances to purify the thus obtained hulupones. Hulupones obtained by the process, optionally in combination with isohumulones provide a beer-soluble product which, as a bitter constituent, has all the taste properties of natural hops.

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## SPECIFICATION

## Process for obtaining hulupones from lupulones

5 The present invention relates to a further develop-  
ment of the process described in British Patent  
Application No. 7921290, with the object of obtaining  
bitter-tasting hulupones from lupulones. In accord-  
10 ance with British Patent Application No. 7921290, an  
isomerised hop product may be obtained by adding  
adsorbents to hop products which contain alpha-  
acids and then treating the mixture in a pressure  
vessel at a supercritical temperature and under a  
15 pressure of from 50 to 80 bars. The isomerised  
product thus obtained is withdrawn from the pres-  
sure vessel in a dry form and the carbon dioxide,  
which causes the isomerisation also acts as a solvent  
and purifying agent. The carbon dioxide issuing  
20 from the pressure vessel contains, as dissolved  
substances, hop oils, soft hop resins, in particular  
beta-acids, and other indistinguishable soft resins.  
Under unfavourable operating conditions, it is also  
possible for small quantities of alpha-acids which  
25 have not been isomerised, to be removed from the  
pressure vessel in dissolved form with the carbon  
dioxide.

According to the present invention it has now  
been found that, by reducing the pressure of the CO<sub>2</sub>  
which is led off from the pressure vessel, a pure,  
30 bitter-tasting hulupone product is obtained from the  
base extract which is precipitated in the pressure  
reduction vessel and of which about half consists of  
lupulones, by the addition of an adsorbent and an  
oxidising agent in conjunction with a further pres-  
35 sure treatment with CO<sub>2</sub>, and also that this pure,  
bitter-tasting hulupone product can be added direct-  
ly to beer or other beverages, including alcohol-free  
beverages, which are to be made bitter either on its  
own or together with other bitter constituents, such  
40 as isomerised alpha-acids which have been obtained  
by the process of British Patent Application No.  
7921290.

The lupulones or beta-acids are those hop resins  
which do not have a bitter taste, which are not  
45 isomerised in the brewing process and which are  
discarded thereafter, unused, together with the  
spent hops. From a quantitative point of view, the  
lupulone fraction of hops is as large as the humulone  
fraction thereof, and there has, therefore, been no  
50 lack of attempts to isolate the lupulones, either in the  
brewery itself or in conjunction with the preparation  
of isohumulones with the aid of organic solvents,  
and then to convert them into bitter-tasting hulu-  
pones.

55 German Patent Specification No. 941,965 de-  
scribes a process in which after the customary  
boiling of hops with wort, the spent hops which have  
been removed are oxidised with a controlled quanti-  
ty of oxygen and are thereby converted into a  
60 bitter-tasting soft resin.

German Auslegeschrift No. 1,300,485 is concerned  
with the conversion of lupulones into hulupones,  
and the hop resins, which have been dissolved in an  
organic solvent, are separated by means of a dilute  
65 aqueous alkaline solution into a lupulone-containing

phase and then oxidised by the passing in of oxygen.

In accordance with the disclosure of German  
Offenlegungsschrift No. 2,217, 135, hulupones may  
be obtained from lupulones by oxidising the hop  
70 resins contained in a liquid alkaline medium with  
gases containing oxygen under the influence of  
visible light.

In accordance with the disclosure of German  
Auslegeschrift No. 2,244,895, lupulones are oxidised  
75 catalytically to give hulupones by using finely di-  
vided noble metals or noble metal oxides as  
catalysts.

In the procedure suggested here, an acceleration  
of the oxidation reaction was also observed in an  
80 alkaline, polar solution by increasing the pressure to  
60 atmospheres gauge and also raising the tempera-  
ture to approximately 100°C. However, because of  
the uncontrolled reaction, a yield of unpurified  
hulupone of only approximately 20% was obtained.

85 All the processes mentioned above have the  
disadvantage that in addition to the desired end  
product, the resulting oxidation products contain  
undesirable by-products and therefore cannot be  
added directly to beer.

90 It is the object of the present invention to obtain a  
bitter-tasting hulupone product in improved yield  
and without the disadvantages of undesirable by-  
products, so that it can be added directly to beer or  
to other beverages.

95 According to the present invention there is pro-  
vided a process for obtaining hop extracts which  
comprises adding adsorbents to hop products which  
contain alpha-acids and ground, crushed or ruptured  
lupulin seeds, or hop products which are in the form  
100 of extracts, treating the mixture obtained with CO<sub>2</sub> in  
a closed pressure vessel at a supercritical tempera-  
ture and under a pressure of from 50 to 600 bars,  
reducing the pressure of the CO<sub>2</sub> leaving the pres-  
sure vessel whereby a base extract comprising hop  
oils and lupulones is precipitated, mixing the lupu-  
105 lones with adsorbents, converting the lupulones to  
bitter-tasting hulupones by oxidation and treatment  
with CO<sub>2</sub> under pressure, and removing undesirable  
accompanying substances to purify the thus  
obtained hulupones. Preferably, hop products in the  
110 form of extracts are used, these extracts most  
preferably being obtained by a process which com-  
prises extracting hops or a hop product with CO<sub>2</sub> at a  
temperature up to its critical temperature and at a  
pressure above its critical pressure and subsequent-  
115 ly evaporating the CO<sub>2</sub> from the extract obtained.

In detail, the process according to the present  
invention may be carried out as follows:

The base extract obtained on the pressure reduc-  
120 tion side in the isomerisation of humulones in  
accordance with British Patent Application No.  
7921290 essentially consists of hop oils, beta-acids  
and indefinable soft resins, esters and waxes. By  
removal in stages, the hop oils are separated in a  
125 nearly pure form from the other constituents of this  
base extract.

This separation is appropriately effected in a  
second pressure reduction vessel which is placed  
downstream, and which reduces the pressure of the  
130 circulating CO<sub>2</sub> by means of a suitably adjusted

pressure reduction valve, to a lower pressure than that in the first pressure reduction vessel.

After isomerisation of the alpha-acid in accordance with the process of British Patent Application No. 7921290 and also removal of the hop oils in the second pressure reduction vessel are complete, the base extract is removed from the pressure reduction vessel.

Instead of a base extract obtained by CO<sub>2</sub> extraction, it is also possible to use extracts obtained in another manner, for example those produced in the isomerisation process with the aid of organic solvents.

In order to enlarge the surface area of the resin-like base extract and also to promote the formation of hulupate salts, the base extract is mixed with adsorbents, as a result of which a pulverulent extract is formed. Suitable adsorbents for use in the present invention are all conventional adsorbents, such as, for example, activated charcoal, activated aluminium oxide. Fuller's earth, sodium bentonite, calcium bentonite, silica gel, kieselguhr and the like and also the known alkali and alkaline earth metal salts and their oxides or hydroxides, which are fixed by lupulones and/or hulupones by adhesion, with salt formation. These include, in particular, Na<sub>2</sub>CO<sub>3</sub>, MgCO<sub>3</sub>, CaCl<sub>2</sub>, calcium oxide, magnesium oxide, sodium hydroxide and also potassium hydroxide.

The base extract which has been mixed with one or more of the aforementioned carriers is also treated with one or more oxidising agents. Oxidising agents suitable for use in the present invention are, besides pure oxygen and the oxygen of the atmosphere, all known oxidants which can be used without leaving a detrimental residue in an end product which is intended for food purposes.

It should be understood that the term liquid CO<sub>2</sub> as used herein means not only carbon dioxide which is subcritical with respect to pressure and temperature, but also carbon dioxide which is sub-critical with respect to its temperature only (that is to say at or below 31.3°C), and which can also definitely have higher pressures than the pressure corresponding to the critical pressure of about 73 bars (for example, a pressure of 200 bars and a temperature of 28°C).

The term supercritical CO<sub>2</sub> as used herein means carbon dioxide which has a temperature higher than 31.3°C and at the same time a pressure higher than 73 bars.

It was surprising to find that the formation of bitter-tasting hulupones, associated with a purification of these hulupones from the aforementioned undesirable and indefinable soft resins, esters and waxes takes place only as a result of the action of liquid or supercritical CO<sub>2</sub>.

This conversion into bitter-tasting hulupones and the purification of the same by means of CO<sub>2</sub> under the conditions of the present invention would not have been expected, since hitherto it was only known that crude hulupones are formed from lupulones in the presence of an alkali and/or oxidising agents. This is especially unexpected since CO<sub>2</sub> is neither an oxidising agent nor a substance with an alkaline reaction.

The pressure treatment with CO<sub>2</sub> according to the

present invention therefore constitutes a conversion of the lupulones into bitter-tasting hulupones and includes the purification of the hulupones thus obtained.

The base extract which has been pretreated by the process of the present invention is conveyed into the extraction vessel of a CO<sub>2</sub> high-pressure apparatus and is there treated with CO<sub>2</sub>, e.g. liquid or supercritical CO<sub>2</sub>. Excess CO<sub>2</sub>, which is charged with the undesirable soft resins, esters and waxes, is continuously discharged into a pressure reduction vessel through a pressure controlled pressure reduction valve.

The action of the circulating CO<sub>2</sub> ensures that, at the end of the extraction, only the bitter-tasting hulupones and/or salts thereof, together with the adsorbents used, are still present in the extraction vessel in the form of a pulverulent substance. The pulverulent hulupones which are removed from the pressure vessel are then subjected to a process of fine comminution and can subsequently be added directly to the finished beer either on their own or else mixed with isoalpha-acids which have been obtained in accordance with the process of British Patent Application No. 7921290. The addition of quantities of hulupones, as compared with the addition of equivalent quantities of isohumulones to beer which was ready for drawing off showed no significant differences in the purity of the odour of the beer, in the purity of its taste, in the intensity and quality of its bitter taste nor in the body of the beer. In terms of the intensity of the bitter taste, the addition of hulupones obtained in accordance with the present invention leads to a saving in the quantity of isohumulones added as a bitter constituent which corresponds to the amount of hulupones added.

The hulupones obtained in accordance with the present invention, in combination with the isohumulones obtained in accordance with the process of British Patent Application No. 7921290, provides a beer-soluble product, as a bitter constituent, which has all the taste properties of natural hops.

#### Example

500 g of base extract which is freed from oil ( $\beta$ -acid content 49% on an anhydrous basis) is mixed with 500 g of sodium bentonite, and the mixture obtained is then treated for 2 hours in a pressure vessel under a pressure of 250 bars by sucking in and blowing out air through two interposed pressure reduction valves.

Subsequently to the above oxidative treatment, the pulverulent base extract present in the pressure vessel is treated for 3 hours by passing there in supercritical CO<sub>2</sub> at 70°C and under a CO<sub>2</sub> pressure of 350 bars.

During this treatment time, the undefinable resins (soft resins and hard resins), waxes and esters which are charged with CO<sub>2</sub> are separated off in portions at a time interval of about every 7 seconds through a pressure reduction valve into a pressure reduction vessel at a pressure of 50 bars and a temperature of 21°C.

The yellow, resin-like mass obtained in the pressure reduction vessel is nearly free from  $\beta$ -acids, while the pulverulent product remaining in the pressure vessel is also free from  $\beta$ -acids.

When dissolved in water, the filtrate from the pulverulent product exhibits an intense and agreeably bitter taste. The substances having the taste have been identified as hulupones by means of thin layer chromatography.

#### CLAIMS

1. A process for obtaining hop extracts which comprises adding adsorbents to hop products which contain alpha acids and ground, crushed or ruptured lupulin seeds, or such hop products which are in the form of extracts, treating the mixture obtained with CO<sub>2</sub> in a closed pressure vessel at a supercritical temperature and under a pressure of from 50 to 600 bars, reducing the pressure of the CO<sub>2</sub> leaving the pressure vessel whereby a base extract comprising hop oils and lupulones is precipitated, mixing the lupulones with adsorbents, converting the lupulones to bitter-tasting hulupones by oxidation and treatment with CO<sub>2</sub> under pressure, and removing undesirable accompanying substances to purify the thus obtained hulupones.
2. A process as claimed in claim 1 wherein hop products in the form of extracts are used.
3. A process as claimed in claim 2 wherein the extracts are obtained by a process which comprises extracting hops or a hop product with CO<sub>2</sub> at a temperature up to its critical temperature and at a pressure above its critical pressure and subsequently evaporating the CO<sub>2</sub> from the extract obtained.
4. A process as claimed in any of claims 1 to 3 wherein the hop oils contained in the base extract are separated from the lupulones by reducing the pressure of the CO<sub>2</sub> in stages.
5. A process as claimed in claim 4 wherein in a first stage the CO<sub>2</sub> pressure is reduced to from 15 to 50% of the pressure prevailing in the pressure vessel, and in a second stage the CO<sub>2</sub> pressure is reduced to from 50 to 80% of the pressure in said first stage.
6. A process as claimed in any of claims 1 to 5 wherein atmosphere oxygen is used as the oxidising agent in the oxidation stage.
7. A process as claimed in any of claims 1 to 5 wherein a suitable oxidant (as herein defined) is used as the oxidising agent in the oxidation stage.
8. A process as claimed in any of claims 1 to 7 wherein adsorbents are added to the base extract for purifying the bitter-tasting hulupones.
9. A process as claimed in any of claims 1 to 8 wherein a pressure treatment with CO<sub>2</sub> in which the pressure of the CO<sub>2</sub> is reduced continuously is carried out for converting the lupulones into bitter-tasting hulupones and for the purification thereof.
10. A process as claimed in any of claims 1 to 9 wherein the conversion of the lupulones into bitter-tasting hulupones and the purification thereof is carried out in the pressure vessel using liquid CO<sub>2</sub>, the pressure of the CO<sub>2</sub> being reduced continuously.
11. A process as claimed in any of claims 1 to 9 wherein the conversion of the lupulones to bitter-tasting hulupones and the purification thereof is carried out in the pressure vessel using CO<sub>2</sub> above

its critical point, the pressure of the CO<sub>2</sub> being reduced continuously.

12. A process as claimed in any of claims 1 to 11 which further comprises the step of adding the hulupones obtained, optionally together with isomerised alpha-acids to an alcohol-containing or an alcohol-free beverage which is to be made bitter.

13. A process for obtaining hulupones substantially as herein described with reference to the Example.

14. Hulupones whenever obtained by a process as claimed in any of claims 1 to 12.

15. Substances whenever obtained by a process as claimed in any of claims 1 to 13.

16. Beer containing hulupones as claimed in claim 14.

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